



Catalytic conversion of hemicellulosic biomass to lactic acid in pH neutral aqueous phase media



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ABSTRACT

The conversion of lignocellulosic biomass into value-added chemicals using non-toxic heterogeneous catalysts and water as solvent is an attractive green process. Biomass-derived lactic acid is an important renewable chemical building block for synthesizing commodity chemicals, e.g. biodegradable plastics. This paper reports that hemicellulosic biomass, xylan and xylose, can be converted to lactic acid over a ZrO_2 catalyst starting from pH neutral aqueous solutions. The effects of reaction conditions, including temperature, oxygen partial pressure, biomass loading, and catalyst loading, etc., on the conversions of hemicellulosic biomass and the corresponding yields of lactic acid have been investigated. Molar yields of lactic acid, up to 42% and 30% were produced from xylose and xylan, respectively, under the investigated reaction conditions and with the ZrO_2 catalyst. The key intermediates such as glyceraldehyde, glycolaldehyde and pyruvaldehyde were used as the reactants to probe the reaction mechanism. The role of the ZrO_2 catalyst in the retro-aldol condensation of xylose, as well as the catalyst stability, has been discussed.

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1. Introduction

Lignocellulosic biomass is a renewable resource with the potential of a billion tons (10^{12} kg) per year supply in the United States [1]. Hemicellulose, along with cellulose and lignin, is presented in almost all plant cell walls of terrestrial biomass species, constituting approximately 20–35% of lignocellulosic biomass [2]. Hemicellulose is a mixture of heteropolymers (matrix polysaccharides), such as arabinoxylans, with a random, amorphous structure that can be readily hydrolyzed with dilute acids [3]. Xylose, a C5 sugar and the monomer of xylan, is one of the most abundant sugars found in nature [4]. Maize is composed of 13–25% xylan by dry weight [5], while beech wood contains approximately 19% xylose [6]. However, xylan and xylose have not yet been fully utilized in industry. In the paper industry, a significant amount of xylose, from the hydrolysis of woody biomass, is mixed with lignin-derived compounds and burned to provide process heat [7]. Although xylose can be fermented to ethanol, commercial enzymes or yeasts are not available in bio-ethanol industry. Thus, although the abundance and ease of isolation make xylose an ideal feedstock for the production of chemicals and fuels, cost-effective conversion processes are essential to fully explore its potential.

Carboxylic acids represent an important class of renewable chemicals derived from biomass. The U.S. Department of Energy released a list of 30 basic molecules that can be derived from carbohydrate biomass to guide the emerging research in production of bio-based chemicals [6]. Bozell et al. has updated this list recently based on criteria used in evaluating biobased product opportunities [8]. In both lists, carbohydrate-derived organic acids (e.g., lactic, succinic, and levulinic acid) are among the “platform-molecules”, which can be further converted into high-value-added chemicals. Among the biomass-derived carboxylic acids, lactic acid is an important renewable chemical building block for the production of biodegradable plastics and has the potential to replace existing petroleum-based materials. Lactic acid is also a platform chemical for synthesizing alternative liquid fuels [9] and other commodity chemicals [10–12] such as propylene oxide (via hydrogenation), acrylic acid (via dehydration), propanoic acid (via reduction), 2,3-pentanedione (via condensation), and ethyl lactate (via esterification). The commercial production of fermentative lactic acid uses glucose or corn starch as the feedstock [13,14]. There are increased concerns of using biomass feedstocks that compete with food for the production of commodity chemicals like lactic acid. Moreover, these biological processes have drawbacks such as costly separation, slow kinetics, and poor scalability [15].

Recently, chemical synthesis routes using biomass resources have emerged for the production of lactic acid. A relatively high yield of lactic acid, up to 27% in terms of carbon mole percentage,

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can be obtained from the hydrothermal conversion of glucose and cellulose by adding homogeneous base catalysts, e.g. NaOH or $\text{Ca}(\text{OH})_2$ [16]. A solvent-free process with the KOH catalyst under microwave irradiation testing various sugar feedstocks found that the yields of lactic acid from C5 sugars such as arabinose (35%) were obviously lower than those from C6 sugars, e.g. glucose (75%) [17]. High-temperature treatments of xylose (200 °C) in a $\text{Ca}(\text{OH})_2$ solution produced ~57 mol% of lactic acid [18]. Bicker et al. found that among the transition metal ions they tested, the Zn^{2+} ion is the best catalyst to produce lactic acid from sucrose or glucose in sub-critical water at 300 °C [19]. Contradictorily, Kong et al. observed that the yields of lactic acid decreased with increasing the concentration of Zn^{2+} ions in the similar hydrothermal media [20]. Although bases and transition metal ions are good catalysts for the production of lactic acid from plant sugars, the disadvantages are that anti-corrosive materials or costly separation are required for catalyst recovery and reuse.

There are a few studies on the conversion of carbohydrates to lactic acid or lactates over heterogeneous catalysts. Chambon et al. found that lactic acid was produced directly from cellulose over heterogeneous Lewis acid catalysts, tungstated alumina and tungstated zirconia, with the carbon mole yields of 27% and 18.5%, respectively [21]. Holm et al. reported that the Lewis acidic zeotype materials, such as Sn-Beta, catalyzed the conversion of mono- and disaccharides to methyl lactate in methanol at 160 °C. With sucrose as the substrate, the methyl lactate yield reached a record high of 68%. However, changing the solvent from methanol to water led to the formation of much lower amounts of lactic acid (<30%) [22]. Solid base catalysts, including hydrotalcites [23] and magnesium oxide [24], and supported noble metal catalysts [25] were also used for catalyzing the formation of lactic acid or methyl lactate from glucose with, however, much lower yields than Sn-Beta. However, there is little study on converting hemicellulose such as xylose and xylan to lactic acid with heterogeneous catalysts.

Herein we report our findings on the catalytic conversion of xylose and xylan to lactic acid using a zirconium dioxide (ZrO_2) catalyst in pH-neutral high-temperature water without adding base or co-solvent. A possible bi-functional acid/base reaction mechanism is proposed that explains why the performance of ZrO_2 is superior compared to MgO , a solid base catalyst, towards the production of lactic acid from xylose.

2. Experimental

2.1. Materials

D-(+)-Xylose (99%), xylan from beechwood (>90%), Glacial acetic acid (99.7%), Bis (trimethylsilyl) trifluoroacetamide (BSTFA)+trimethylchlorosilane (TMCS) (99:1), D-(+)-glyceraldehyde (98%), glycolaldehyde dimer, glycolic acid, L-(+)- lactic acid (98%), oxalic acid (99.0%), 2-hydroxybutyric acid (97%), propionic acid (99.5%), acrylic acid (99%), pyridine anhydrous (99.8%), pyruvaldehyde (40 wt% solution in water), furfural (99%), 5-(hydroxymethyl) furfural (99%), sulfuric acid (98%), and magnesium nitrate hexahydrate (99%) were purchased from Sigma Aldrich. Formic acid (98%) was purchased from Fluka. Sodium hydroxide (ACS reagent) was purchased from Mallinckrodt Chemicals. Zirconium oxide catalyst was purchased from Alfa Aesar and calcined at 250 °C for 2 h before use. Magnesium oxide catalyst was attained by calcining magnesium nitrate hexahydrate at 550 °C in air for 3 h.

2.2. Catalytic reactions

All reactions were carried out in a 100 mL stirred Parr microreactor. In a typical run, solid catalyst and xylose/xylan were added

into 20 mL deionized water in a glass liner placed in the reactor. The Parr reactor was then sealed, purged with high purity nitrogen (99.99%), and then charged with reactive gases to the set pressure. The reactor was heated at a ramp rate of 10 °C/min until the desired temperature was reached. During the reaction, mixing was achieved through an internal propeller operating at 800 RPM. Once the set temperature was attained, the reactor was held for the set reaction time, and then quenched quickly in an ice bath to stop the reaction. The reactor was cooled until approximately 25 °C, and then vented after the gas pressure was recorded. The reactor was immediately broken down and the solid residue remaining in the reactor was recovered and dried for the calculation of solid residue yields. The aqueous and solid fractions were separated using a centrifuge. The weights of liquid portion and dried solid residues were recorded. The mass balance was calculated and was ensured to be between 98% and 102%.

The S.R. yield (solid residue yield), the product yield, and the TOC yield (total organic carbon yield) are calculated using the following equations:

$$\text{S.R. yield} = \frac{\text{weight of total dried solid residue} - \text{weight of solid catalyst}}{\text{weight of hemicellulosic biomass feedstock}}$$

$$\text{Product yield} = \frac{\text{mole of aqueous phase product}}{\text{mole of hemicellulosic biomass feedstock}}$$

$$\text{TOC yield} = \frac{\text{carbon weight of all aqueous phase products}}{\text{carbon weight of hemicellulosic biomass feedstock}}$$

For the catalyst stability tests, the spent catalyst was collected and dried overnight in an oven at 105 °C, and then was reused under the same reaction conditions. Due to the collection loss, the actual weight of the catalyst was slightly lower than the initial weight and the corresponding biomass loading was reduced to keep the constant weight ratio of catalyst to biomass.

2.3. Product analysis

The liquid product of each reaction was characterized by a Shimadzu high performance liquid chromatography (HPLC), an Agilent gas chromatography/mass spectrometry (GC/MS), a Shimadzu total organic carbon analyzer (TOC), a Waters electron spray ionization mass spectrometry (ESI/MS), and a Bruker nuclear magnetic resonance spectrometry (NMR).

The aqueous solution after reaction was filtered through a 0.45 μm syringe filter and then diluted 15 times with ultra-pure water. HPLC analysis was performed using a Shimadzu HPLC system equipped a UV–vis Detector (Shimadzu SPD 10-AV) and Refractive Index Detector (Shimadzu RID-6A). For analysis of organic acids and reaction intermediates, the samples were separated in an Aminex 87-H column from Bio-Rad, using 5 mM H_2SO_4 as the mobile phase, 0.7 mL/min flow, at a column temperature of 55 °C. For quantitative identification and results, the UV–vis detector was utilized at 208 nm and 290 nm. However, the peaks of lactic acid and glycolic acid were overlapped under the UV–vis detector. Thus the refractive index detector was used to quantify the yields of lactic acid and glycolic acid.

Derivatization of the polar components was performed in order to perform qualitative GC/MS analysis and identification of unknown components in the aqueous phase. For a silylation derivatization, 125 μL liquid were lyophilized overnight in deactivated 1.5 mL vials. To the dried solids, 100 μL of acetonitrile was added and mixed to allow the solids to dissolve, and then 50 μL of pyridine and 100 μL of BSTFA with TMCS (99:1) were added. The capped vials were placed in a water bath maintained at 65 °C for 2 h to allow complete silylation. After silylation, the samples were cooled and a 100 μL mixture was taken to be diluted with 1.4 mL of

dichloromethane. The sample were injected in Agilent 6890 series GC/MS equipped with an Agilent DB5-MS column (30 m \times 0.25 mm ID, 0.25 μ m film thickness) and Agilent 5973 mass selective detector. The column temperature was maintained at 100 °C.

After the reaction, the resultant aqueous phase product samples were also prepared for total organic carbon analysis (TOC). For TOC analysis, the aqueous phase after reaction was filtered through a 0.45 μ m syringe filter then diluted 200 times with ultra-pure water. TOC was measured by a Shimadzu Total Organic Carbon Analyzer (model TOC-VCSH). The TC standard was prepared by reagent grade potassium hydrogen phthalate, the IC standard was prepared by reagent grade sodium bicarbonate and sodium carbonate. The carbon concentration of the standard solution corresponds to 1000 mg C/L. The standard stock solution was diluted with ultra-pure water to 100 ppm C.

All samples were detected by NMR chromatogram with a Varian model number NMR V500 using DMSO as solvent. Before the test, all samples were dried in the freeze dry system in order to get rid of water in the samples.

For ESI/MS measurement, all samples were diluted by base solution and tested by ESI on Water e2695 operated on a negative mode. The base solution was prepared by adding 1 g triethylamine into 1 L ultra-pure water. Then the sample solution was diluted with the base solution to 100 ppm. The source and desolvation temperature were 130 °C and 250 °C, respectively. The pump flow rate was 10 μ L/min.

2.4. Catalyst analysis

Temperature-programmed desorption (TPD) of adsorbed CO or CO₂ on catalysts was carried out using a Micromeritics AutoChem II 2920 Chemisorption Analyzer. Each experiment was initiated by pre-treating the catalyst sample in pure O₂ flowing at 100 cm³/min for 2 h at 873 K. The sample was then flushed in helium and cooled to the desired adsorption temperatures, 523 K and 273 K for CO and CO₂, respectively. CO was adsorbed on the catalysts by flowing a 4% CO in helium stream for a total time of 20 min, while CO₂ was adsorbed on the catalysts by flowing a 10% CO₂ blended in helium stream for a total time of 40 min. The sample was then cooled to room temperature and flushed with helium for 30 min. Temperature-programmed desorption was carried out in flowing He (100 cm³/min) with a heating rate of 25 K/min and 10 K/min for CO and CO₂, respectively, from 300 K to 700 K.

The infrared (IR) spectroscopy by the Attenuated total reflectance (ATR) was used to characterize surface functional groups on the ZrO₂ catalyst before and after the xylose conversion reactions. The ATR-FTIR spectroscopy was recorded on the Thermo Scientific Nicolet 6700 FT-IR equipment with the 16 scans number. The background spectrum was recorded first to remove the air effect before the sample test.

3. Results and discussion

3.1. Conversion of xylose to lactic acid

Fig. 1 compares the yields of major products by reacting xylose at different reaction temperatures while other operating conditions were kept identical. The inset in Fig. 1 shows the solid residue yields (S.R.) and the total organic carbon (TOC) yields in aqueous phase. The pronounced effect of temperature on converting xylose to lactic acid was obvious: the lactic acid yield consistently increased with the increase of temperature. However, the lactic acid yields varied little at temperatures above 200 °C, although the maximum lactic acid yield was achieved at 240 °C. In contrast, as shown in Fig. 2, the lactic acid yields decreased as the oxygen partial pressure increased

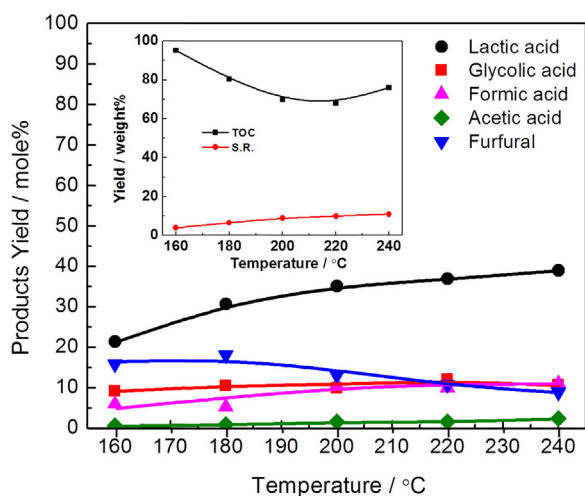


Fig. 1. Temperature effect on the yields aqueous-phase products of xylose conversion with the ZrO₂ catalyst in pH neutral aqueous solution. The inset figure shows the temperature effect on the solid residue yields and the TOC yields in the same reaction. Reaction conditions: 40 min, 2.4 MPa N₂, 0% O₂, 5 wt% xylose loading, and 0.8:1 mass ratio of catalyst to xylose.

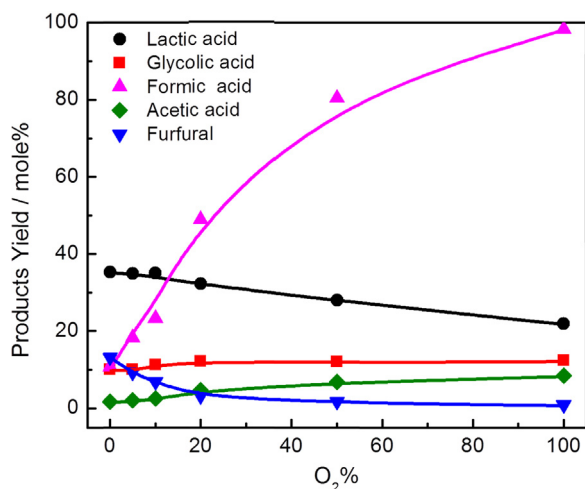


Fig. 2. Effect of O₂ partial pressure on the yields of the aqueous-phase products by the conversion of xylose with the ZrO₂ catalyst in pH neutral aqueous solutions. Reaction conditions: 200 °C, 40 min, 2.4 MPa N₂ + O₂, 5 wt% xylose loading, and 0.8:1 mass ratio of catalyst to xylose.

and the maximum yield of lactic acid was obtained with 0% O₂. Lactic acid can be further degraded to formic acid, acetic acid, or CO₂ by oxidation. As seen in Fig. 2, the yield of formic acid significantly increased as the O₂ partial pressure increased from 0% to 100%. With increasing O₂ partial pressure from 0% to 20%, the yield of furfural decreased rapidly. When the O₂ partial pressure was larger than 20%, furfural was almost completely decomposed. In contrast, there were negligible changes in lactic acid yields in the operation range of the O₂ partial pressures from 0% to 10%. The catalyst loading effect on xylose conversion was shown in Fig. 3. Without adding the ZrO₂ catalyst, the main product was furfural through the dehydration of xylose in high-temperature water. The lactic acid yield rapidly increased to 30% when adding 0.5 g ZrO₂, i.e., at the catalyst to xylose ratio of 0.5. The highest lactic acid yield of 42.5% was achieved when the ratio of ZrO₂ to xylose was 2:1. However, the lactic acid yield varied little as the catalyst loading was above 1 g. Other carboxylic acids such as glycolic acid and formic acid followed the same trend as lactic acid. Contrarily, the furfural yield consistently decreased with increasing the ZrO₂ loading

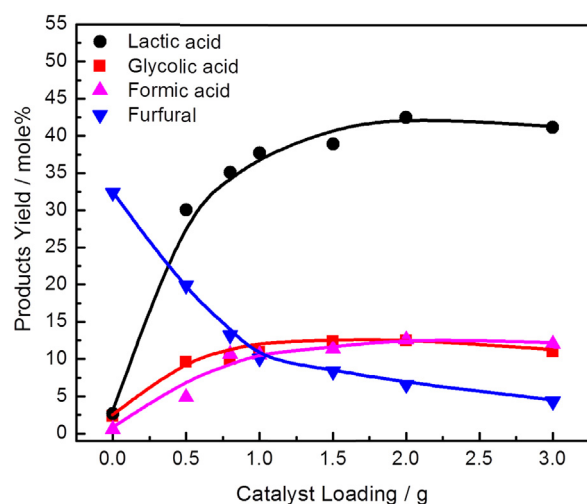


Fig. 3. Effect of catalyst loading on the yields of the aqueous-phase products by the conversion of xylose with the ZrO_2 catalyst in pH neutral aqueous solutions. Reaction conditions: 200 °C, 40 min, 2.4 MPa N_2 , 0% O_2 , 5 wt% xylose loading, and 0.8:1 mass ratio of catalyst to xylose.

amount. To confirm the identification of the major aqueous-phase compounds, electron spray ionization mass spectrometry (ESI-MS), nuclear magnetic resonance (NMR), and gas chromatography coupled with mass spectrometry (GC/MS) were used. Fig. S1 displayed an ESI-MS total ion chromatogram in the regions of m/z 30–160 and the signals of lactic acid, glycolic acid, formic acid, and acetic acid were observed. As shown in Fig. S2, the ^{13}C NMR spectra of lactic acid in the reaction products matched well with the standards. The GC/MS spectra also confirm the major aqueous phase products, as shown in Fig. S3. Overall, a relatively high yield of lactic acid from xylose can be achieved under mild reaction conditions when using a ZrO_2 as the heterogeneous catalyst.

To further investigate the catalytic effect of ZrO_2 , a mono-functional solid base catalyst, MgO, was chosen to compare with ZrO_2 . Different pH values were deliberately adjusted at the beginning of the reaction. The yields of major aqueous-phase products were compared with and without the catalysts, as shown in Table 1. It was found that 32.4% of furfural but no lactic acid was formed in the neutral aqueous solution without adding any acid or base catalyst (Table 1, Entry 13). With dilute sulfuric acid (pH3) as catalyst, 48.3% furfural was obtained (Table 1, Entry 12), while 73.9% lactic

acid was formed using 1 mol/L sodium hydroxide (pH 14) as the catalyst (Table 1, Entry 15), which were comparable with the literature reported data [26]. Interestingly, ZrO_2 gave the higher yield of lactic acid than MgO in neutral or weakly acidic/basic aqueous solutions. An average lactic acid yield of $35.2 \pm 2.5\%$ was obtained with the ZrO_2 catalyst in the neutral aqueous solution (Table 1, Entry 3). In contrast, lactic acid with a lower yield, $\sim 22.9\%$, was produced over MgO (Table 1, Entry 8) under the same conditions. The lactic acid yields appeared to be insensitive to the pH in the range of 3 to 10, with either ZrO_2 or MgO as the catalyst. Unlike ZrO_2 , the MgO catalyst yielded no furfural but a higher amount of low molecular-weight carboxylic acids including formic, acetic and glycolic acids in the pH range of 0 to 14. The formation of acetic acid may stem from a hydrolytic β -cleavage by the nucleophilic attack of the base [27]. Alkaline earth metal oxides such as MgO are strong solid base catalysts [28], resembling the homogeneous base catalyst in terms of a similar product distribution, while MgO yielded lower amounts of lactic acid and glycolic acid than NaOH. The performance of homogeneous catalysts, by virtue of lower mass transfer resistance and higher accessibility of catalytic active sites, is usually found to be superior to that of solid catalysts. However, the reaction pathway using the ZrO_2 catalyst is obviously different from that using a mono-functional base catalyst like MgO. Besides yielding noticeable furfural, the ZrO_2 catalyst even yielded a higher amount of lactic acid and lower amounts of acetic acid and formic acid. The yield of lactic acid followed an opposite trend compared to that of furfural with temperature and catalyst loading amount. To determine whether or not furfural is the key intermediate to produce lactic acid, we examined furfural as the reactant under the same conditions that xylose reacted. No lactic acid was produced with furfural as feedstock (Table S1), suggesting that a dehydration step is unnecessary for lactic acid production over the ZrO_2 . It is widely accepted that Brønsted acids catalyze the dehydration of xylose to produce furfural [29], while bases catalyze retro-aldol condensation leading to the formation of lactic acid from glucose or xylose [30]. Herein, ZrO_2 is the only mono-metal oxide with all four different properties: acidic, basic, oxidative and reductive [31]. The co-existence of furfural and lactic acid in the final products indicates that both the acidic and basic sites on ZrO_2 function during the xylose conversion reactions. However, it is unclear whether or not the acid and base functionalities on the same ZrO_2 catalyst would affect each other and thus cause either suppression or promotion of a specific reaction to produce lactic acid from xylose.

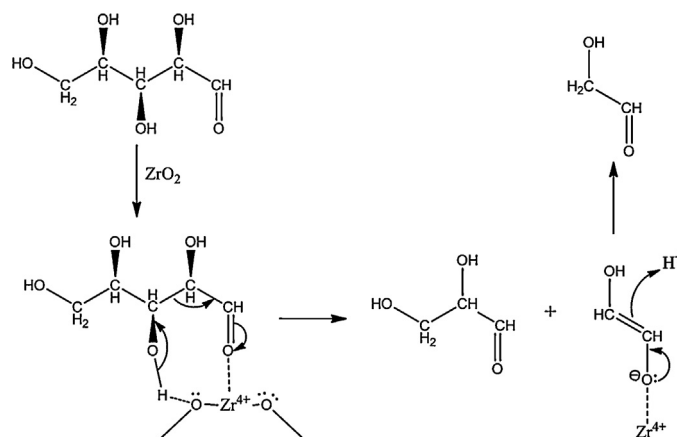
Table 1
Comparison of different catalysts and pH values towards the xylose conversion in aqueous solutions.

Entry	Catalyst	pH	S.R. (%)	Molar yields of aqueous-phase products ^a							
				Ox. (%)	Gly. (%)	Lac. (%)	FA (%)	2-HB (%)	AA (%)	Acrylic (%)	Furfural (%)
1	ZrO_2	0	23	0.09	7.9	0.0	15.8	0.3	1.3	0.01	10.7
2	ZrO_2	3	11	0.02	10.5	36.0	7.6	0.4	2.0	0.00	13.3
3 ^b	ZrO_2	7	9	0.40	10.0	35.2	10.6	0.5	1.7	0.14	13.2
4	ZrO_2	10	14	0.01	10.0	35.3	7.9	0.4	1.6	0.09	11.4
5	ZrO_2	14	17	0.88	28.4	73.7	39.3	0.0	7.6	0.27	0.0
6	MgO	0	15	0.68	16.7	26.6	17.3	0.2	8.7	0.20	0.0
7	MgO	3	12	0.60	15.4	22.2	16.0	0.1	10.0	0.23	0.0
8	MgO	7	21	0.48	15.0	22.9	15.1	0.1	10.8	0.22	0.0
9	MgO	10	23	0.52	15.6	23.8	15.3	0.1	11.2	0.22	0.0
10	MgO	14	52	0.36	29.1	73.8	41.7	0.0	7.9	0.30	0.0
11	H_2SO_4	0	40	0.06	3.4	0.0	15.6	0.0	1.3	0.01	9.4
12	H_2SO_4	3	13	0.00	1.2	0.0	0.0	0.0	0.7	0.09	48.3
13	No catalyst	7	15	0.11	2.3	2.7	0.6	0.0	0.6	0.06	32.4
14	NaOH	10	13	0.01	2.2	2.0	0.0	0.0	0.4	0.05	33.2
15	NaOH	14	37	0.67	28.7	73.9	38.4	0.0	8.1	0.28	0.0

^a Reaction conditions: 40 min, 2.4 MPa N_2 , 0% O_2 , 5 wt% xylose loading, and 0.8:1 mass ratio of catalyst to xylose. Abbreviation: Ox: oxalic acid; Gly: glycolic acid; Lac: lactic acid; FA: formic acid; 2-HB: 2-hydroxybutyric acid; AA: acetic acid.

^b Data reported are the mean values of three replicates with $\pm 2.5\%$ error.

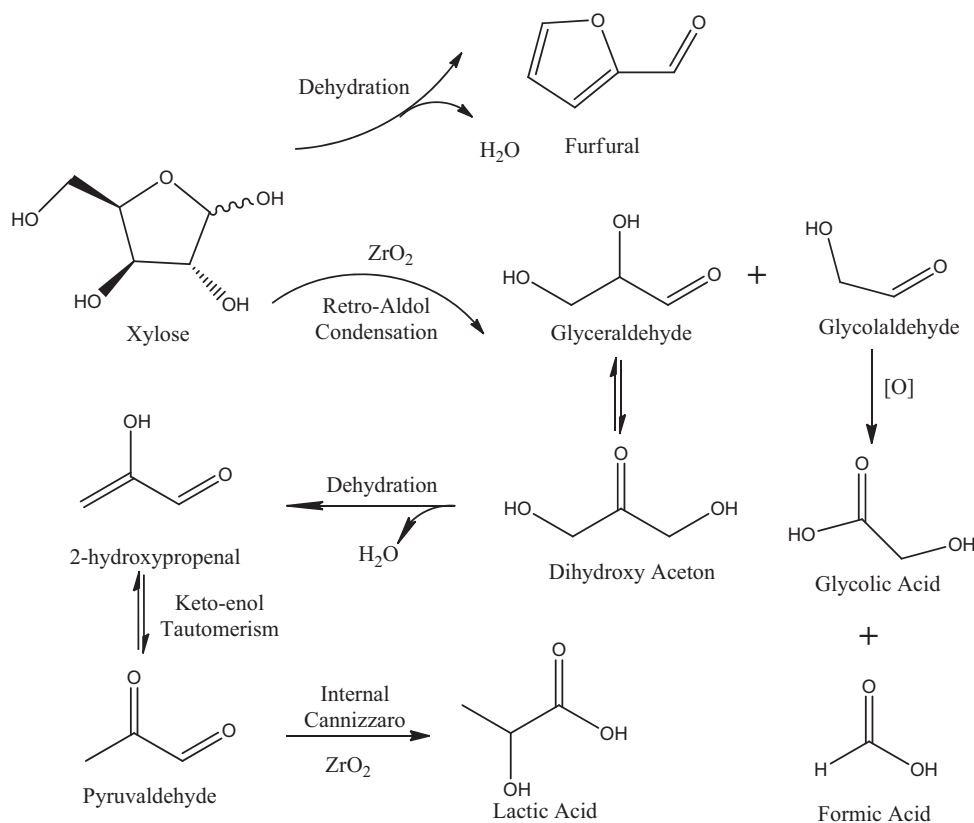
We speculate that the reaction pathway of converting xylose to lactic acid over the ZrO_2 catalyst starts from the retro-aldol condensation to form glycolaldehyde and glyceraldehyde. In the pH neutral hydrothermal media, we did not observe a high yield production of lactic acid (only 2.7%) without adding the ZrO_2 catalyst, while the yield of furfural (32.4%) is instead significantly higher (Table 1, Entry 13). Thus we conclude that the catalytic effects of the free hydroxyl ions from the auto-dissociation of subcritical water are negligible towards the formation of lactic acid from xylose. We tentatively ascribe the bi-functional Lewis acid/base pair on the ZrO_2 surface to catalyzing the retro-aldol condensation of xylose. As shown in Scheme 1, we propose that Zr^{4+} ions as the Lewis acid sites interact with the carbonyl group of xylose, increase the positive charge on carbonyl carbon, and facilitate the nucleophilic attack [32–34]. At the same time, the Lewis acid sites increase the acidity of the active OH group at the position of C-3 carbon, and promote the deprotonation by the weak base, i.e. the O^{2-} cations on the ZrO_2 surface. Thereafter the C–C bond between C-2 and C-3 carbons of xylose is cleaved leading to the formation of glyceraldehyde and glycolaldehyde. Glyceraldehyde may undergo the dehydration to form 2-hydroxypropenal, then to pyruvaldehyde through keto-enol tautomerization, and finally to lactic acid, as shown in Scheme 2. In the presence of a strong base catalyst like concentrated NaOH, α -keto aldehydes can be converted to hydroxy acids in excellent yields via an intramolecular disproportionation, i.e., Cannizzaro reaction [35]. However, Lewis acids are also considered to be capable of catalyzing the intramolecular Cannizzaro reaction by activating the carbonyl function group of the aldehyde, allowing the nucleophilic attack by an electron donor and then an intramolecular rearrangement with a shift of the hydride [20,36]. Hara et al. found that water-tolerant Lewis acids such as $\text{Sc}(\text{OTf})_3$ and $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ can effectively catalyze the hydride



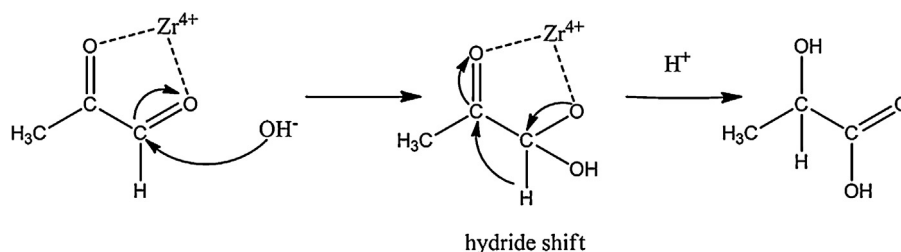
Scheme 1. Proposed reaction mechanism of xylose retro-aldol condensation with the ZrO_2 catalyst. Xylose is converted to glyceraldehyde and glycolaldehyde via the C–C bond cleavage.

transfer of pyruvaldehyde in water by Meerwein–Ponndorf–Verley (MPV) reduction under mild reaction conditions [37]. We thus propose that the transformation of pyruvaldehyde to lactic acid is via the intramolecular Cannizzaro reaction catalyzed by Lewis acid sites on ZrO_2 instead of a strong base, as shown in Scheme 3. Free OH^- and H_3O^+ ions from the auto-dissociation of water are prevailing in subcritical water [38,39]. It is also reported that water can be dissociated on ZrO_2 [40,41]. We thus speculate that the cycle of intramolecular Cannizzaro reaction is closed with the aid of free or surface bound hydroxyl and hydronium ions.

To validate our hypothesis, the possible key intermediates from xylose, e.g. glyceraldehyde and pyruvaldehyde, were used as the



Scheme 2. Proposed reaction mechanism for conversion of xylose to lactic acid and other intermediate and final products in subcritical water with the bi-functional ZrO_2 catalyst.



Scheme 3. Proposed reaction mechanism of converting pyruvaldehyde to lactic acid via intramolecular Cannizzaro with the ZrO_2 catalyst. Lewis acids (Zr^{4+}) activates the carbonyl function groups of the pyruvaldehyde, following the nucleophilic attack by the electron donor (OH^-), then the intramolecular rearrangement with a shift of the hydride, and finally the protonation to form the hydroxyl group at the C2 position.

probe reactants. It shows that these possible key intermediates were readily converted to lactic acid in much higher yields: 50.5% (Table 2, Entry 3) and 93.3% (Table 2, Entry 7) from glyceraldehyde and pyruvaldehyde, respectively, than a lower yield of 40.1% (Table 2, Entry 1) from xylose. Yet in the absence of ZrO_2 , much lower amounts of lactic acid were produced with glyceraldehyde or pyruvaldehyde as the feedstock. In addition, using glycolaldehyde as the probe, far less than the stoichiometric amount of glycolic acid was produced, while a large amount of formic acid was formed and. Glycolaldehyde can be converted to glycolic acid, similar to the conversion of acetaldehyde to acetic acid. However, glycolic acid may be further converted into methanol and CO_2 through cleavage of the C–C bond. As shown in Fig. S4, the GC/MS spectra of the aqueous products from reacting glycolaldehyde in the presence of the ZrO_2 identified a considerable amount of higher molecular-weight compounds such as C4 hydroxyl acids, C6 aldoses, as well as C7 methyl esters. While without adding ZrO_2 , glycolic acid is the dominant product. The formation of higher molecular weight compounds from glycolaldehyde may be through aldol-condensation reactions, which competed against the formation of glycolic acid on the ZrO_2 surface.

To confirm the Lewis acid functionality of the ZrO_2 catalyst, the temperature-programme desorption (TPD) profiles were conducted by using CO as the adsorbate molecule. The comparison of the CO TPD spectra of ZrO_2 and MgO at temperatures from 300 K to 700 K are shown in Fig. 8. A large CO desorption peak at 608 K was observed on ZrO_2 , while no peaks was found on MgO, indicating that the existence of much stronger Lewis acid sites on ZrO_2 although we cannot rule out the existence of very weak Lewis acid sites on MgO. We have tentatively attributed the Lewis acid functionality of the ZrO_2 catalyst to the promotion of retro-aldol condensation of xylose and the intramolecular Cannizzaro reaction of pyruvaldehyde, leading to the formation of lactic acid. There is a wealth of information in literature on NH_3 and CO_2 TPD

characterizing the Brønsted acidity and basicity of ZrO_2 surface [42–45]. The adsorbed pyridine FTIR studies also confirmed the presence of basic sites on the surface of ZrO_2 [45,46]. In this work, the TPD of CO_2 was also carried out in the temperature range from 300 K to 800 K to compare the basicity of ZrO_2 and MgO. A large CO_2 desorption peak at 370 K and two other peaks at 530 K and 590 K were observed on MgO while only one peak at 380 K was found on ZrO_2 , indicating that the existence of much stronger basic sites on MgO. The results are in good agreement with the literature data. However, the sole base function cannot explain why the higher yields of lactic acid were obtained over ZrO_2 than over MgO under our test reaction conditions since MgO has a stronger basicity based on the CO_2 TPD results.

Recyclability and reusability are of importance for heterogeneous catalysts. We thus performed the stability study on the ZrO_2 catalyst. The same catalyst without regeneration was recycled and reused for the subsequent runs under identical reaction conditions. The yields of lactic acid and furfural from xylose using the recycled ZrO_2 catalyst are shown in Fig. 4. Over the five consecutive runs, a slight decline in lactic acid yield, from 34.8% to 29.5%, was found with the re-used ZrO_2 catalyst. This suggests that the catalyst is relatively stable, although a regeneration process that removes the organic solid residues would be desirable for the re-use of the ZrO_2 catalyst. It is interesting that the furfural yield increased with increasing catalyst re-use cycles. It is well known that furfural can be produced through Brønsted acid catalyzed dehydration of xylose. Weak Brønsted acid sites were found on a ZrO_2 surface based on the infrared spectra of adsorbed pyridine [47]. Herein, the deposition of the xylose-derived solid residues on the spent ZrO_2 catalysts may change the surface properties and introduce a higher amount or stronger Brønsted acid sites than the fresh ZrO_2 , thus promoting the dehydration reaction. As shown in the ATR-FTIR spectra (Fig. 5), the spent ZrO_2 catalyst obviously shows the signal of adsorbed species: (1) the broad peak at around 3400 cm^{-1} is

Table 2
Comparison of different biomass derived molecules as the probe reactants which are also possible key intermediates during the catalytic conversion of xylose to lactic acid with the ZrO_2 catalyst.

Entry	Probe	Catalyst	S.R. (%)	Conv. (%)	Molar yields of aqueous-phase products ^a							
					Ox. (%)	Gly. (%)	Lac. (%)	FA (%)	AA (%)	Acrylic (%)	Furfural (%)	HMF (%)
1 ^b	Xylose	ZrO_2	3	100	0.05	11.2	40.1	11.7	0.7	0.2	15.1	0.0
2	Xylose	/	13	78	0.01	0.0	0.0	0.0	0.6	0.07	42.0	0.0
3	D-Glyceraldehyde	ZrO_2	2	100	0.00	0.0	50.5	4.9	5.2	0.01	0.0	0.4
4	D-Glyceraldehyde	/	21	100	0.01	0.0	5.9	6.3	9.9	0.00	0.0	0.03
5	Dihydroxy acetone	ZrO_2	8	100	0.3	0.0	48.7	1.0	2.3	2.6	0.0	0.9
6	Dihydroxy acetone	/	30	100	0.01	0.0	12.5	2.8	6.2	0.00	0.0	1.4
7	Pyruvaldehyde	ZrO_2	4	100	0.00	0.0	93.3	1.3	7.5	0.05	0.0	0.08
8	Pyruvaldehyde	/	23	100	0.01	0.0	7.4	4.7	8.3	0.03	0.0	0.3
9	Glycolaldehyde dimer	ZrO_2	5	100	0.01	4.2	0.0	18.9	0.0	0.00	0.0	1.2
10	Glycolaldehyde dimer	/	19	100	0.00	6.0	0.0	8.0	0.0	0.00	0.0	1.2

^a Reaction conditions: 40 min, 2.4 MPa N_2 , 0% O_2 , 2.5 wt% probe reactant loading, and 0.8:1 mass ratio of catalyst to probe reactant. Abbreviation: Ox: oxalic acid; Gly: glycolic acid; Lac: lactic acid; FA: formic acid; AA: acetic acid; HMF: 5-hydroxy methylfurfural.

^b Data reported are the mean values of two replicates with $\pm 1.3\%$ error.

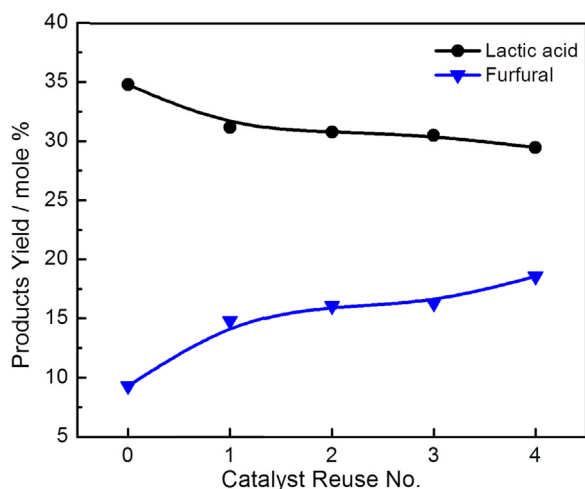


Fig. 4. Effect of re-use of the ZrO_2 catalyst on the yields of lactic acid and furfural by the conversion of xylose in pH neutral aqueous solutions. The spent catalyst was not regenerated. Reaction conditions: 200 °C, 40 min, 2.4 MPa $\text{N}_2 + \text{O}_2$ pressure, 5% O_2 , 5 wt% xylose loading, and 0.8:1 mass ratio of catalyst to xylose.

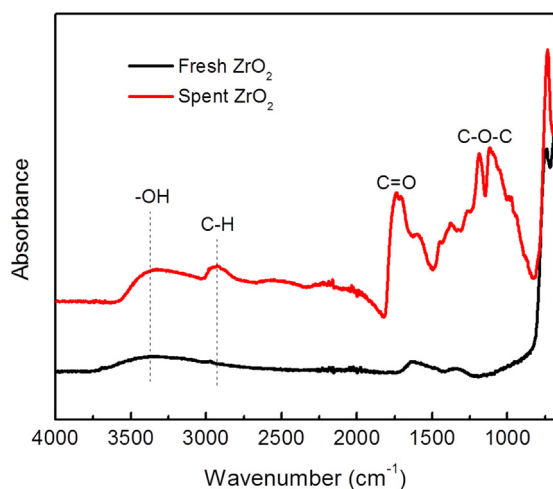


Fig. 5. Comparison of the ATR-FTIR spectra of the fresh and spent ZrO_2 catalysts. The spent catalyst was used once and was not regenerated. Reaction conditions: 200 °C, 40 min, 2.4 MPa N_2 , 5 wt% xylose loading, and 0.8:1 mass ratio of catalyst to xylose.

attributed to the stretching of the OH band; (2) the peaks at around 2980 to 2840 cm^{-1} are the stretching vibration signal of the CH band in $-\text{CH}_2-$ or $-\text{CH}_3$ groups; (3) the twin peaks located at 1750 and 1710 cm^{-1} are probably the C=O band stretching vibrations in acid anhydride molecules [48]; (4) the band at around 1380 cm^{-1} belongs to the CH_3 deformation vibrations [49,50]; and (5) the bands at 1190 and 1120 cm^{-1} may be attributed to the C–O–C band in the acid anhydride molecule [48]. Therefore the enhanced Brønsted acidity, attributing to the increase of the furfural yields and the decrease of the lactic acid yields, may be originated from the carboxylic acid anhydride groups on the surface of the spent ZrO_2 catalysts.

3.2. Direct conversion of xylan to lactic acid

The conversion of xylan into lactic acid was significantly more challenging than was the transformation of water-soluble xylose due to the depolymerization of xylan requiring an intense treatment. Acid hydrolysis is widely used to depolymerize xylan and produce xylose. To further convert xylose to lactic acid, a base catalyst is commonly used. Therefore, direct converting xylan to lactic

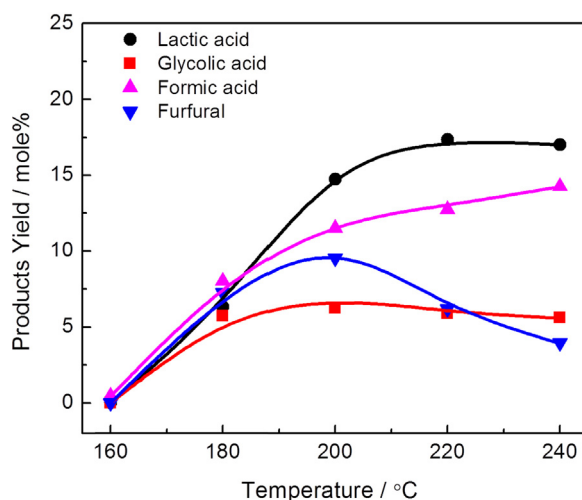


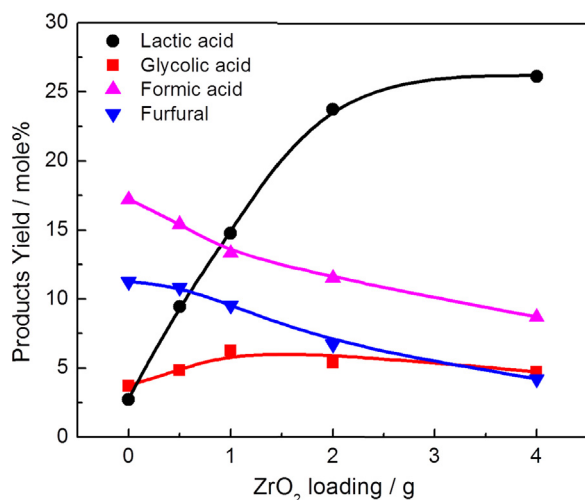
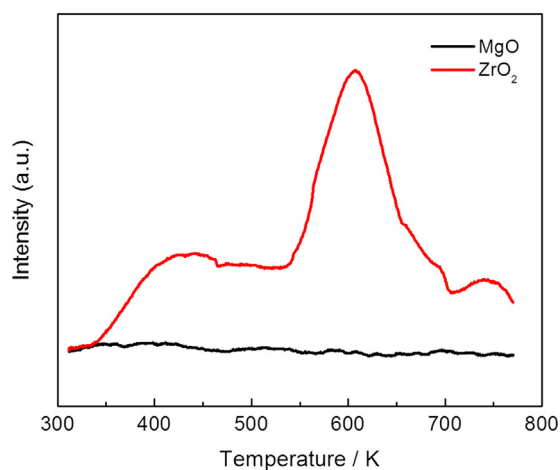
Fig. 6. Effect of temperature on the yields of aqueous-phase products from the xylan conversion with the ZrO_2 catalyst in pH neutral aqueous solution. Reaction conditions: 60 min, 2.4 MPa N_2 , 5 wt% xylan loading, and 1:1 mass ratio of catalyst to xylan.

acid would not be realized if using a homogeneous catalyst system as acids and bases neutralize each other in aqueous solutions. However, it is reasonable to hypothesize that a heterogeneous catalyst system with both the acidic and basic sites on different surface domains would catalyze the conversion of xylan to lactic acid in a one-pot process. To illuminate the effects of acid/base dual functionalities of the ZrO_2 , Beech wood xylan was selected as the model hemicellulosic biomass feedstock for further studies. A Box–Behnken design was used to investigate the influence of process conditions including temperature, reaction time, O_2 partial pressure, and catalyst loading amount, as well as their interactions. Table S2 displays the Box–Behnken experimental results for the yields of the aqueous products, as well as the TOC with xylan as the feedstock under various reaction conditions. The data analysis revealed that temperature and catalyst loading amount had the greatest effects on xylan conversion. Practically, less lactic acid was formed when the catalyst level was low even at high temperatures. Contrarily, at a high ratio of ZrO_2 to xylan, a significant amount of lactic acid was formed even at the low reaction temperature of 180 °C. Reaction time also appeared to be a variable that affects the lactic acid yield, and the longer reaction times, the higher yields. At 190 °C, the highest lactic acid yield of 30% was obtained with the ratio of 3 g ZrO_2 to 1 g xylan and under 10% O_2 partial pressure among all experimental runs. By quickly identifying the most sensitive reaction parameters on lactic acid yield, a detailed temperature and catalyst loading profiling study was performed. Fig. 6 shows that below 180 °C, lactic acid yield is negligible while a lactic acid yield of ~17.3% was obtained at 220 °C. Fig. 7 illustrates the considerable effect of the catalyst loading on the yield of lactic acid from xylan. Without a ZrO_2 catalyst, almost no lactic acid was formed while, under identical conditions, ~26% lactic acid was produced from xylan with adding the ZrO_2 catalyst at to 4:1 ZrO_2 to xylan ratio.

The conversion of xylan is complicated, involving many competing and reversible reactions [51]. Xylan contains as many as 0.659 acetyl groups per xylose unit and thus may be the source of acetic acid in this process. According to Garrote's study [52], the hydrolysis of xylan in hydrothermal media was greatly affected by the acetyl groups in xylan. Ignatchenko and coworkers [53,54] confirmed by DFT computation that the acetyl group can be easily adsorbed on monoclinic zirconia ($-1\ 1\ 1$) and $(1\ 1\ 1)$ surfaces, which may block the access of other reactant molecules. We tentatively

Table 3Effect of acetyl group in the different probe additives, ethyl acetate or acetic acid, on the catalytic conversion of xylose with the ZrO₂ catalyst.

Entry	Probe	S.R. (%)	Molar yields of aqueous-phase products ^a				
			Glycolic (%)	Lactic (%)	Formic (%)	Acrylic (%)	Furfural (%)
1	/	9	10.0	35.2	10.6	0.14	13.2
2	Ethyl acetate	16	9.3	33.7	8.2	0.16	12.4
3	Acetic acid	17	10.9	30.1	12.3	0.09	12.6

^a Reaction conditions: 40 min, 2.4 MPa N₂, 0% O₂, 5 wt% xylose loading, 0.1 g probe additive, and 0.8:1 mass ratio of catalyst to xylose.**Fig. 7.** Effect of catalyst loading on the yields of aqueous-phase products from the xylan conversion with the ZrO₂ catalyst in pH neutral aqueous solution. Reaction conditions: 200 °C, 90 min, 2.4 MPa N₂, 5 wt% xylan loading.**Fig. 8.** Temperature-programmed desorption profile of CO on ZrO₂ and MgO.

relate the presence of acetyl groups in xylan to the lower lactic acid yields with xylan as the feedstock compared to those using xylose as the feed. A doping study was performed to verify the acetyl group effect on xylan. Acetic acid and ethyl acetate, as probes, were deliberately added into the xylose conversion reaction system, respectively. Table 3 shows that the yields of lactic acid from xylose slightly decreased from ~35% to ~34% or ~30% with adding ethyl acetate or acetic acid, respectively, implying that the acetyl group may only slightly affect the catalyst activity. On the other hand, under the same reaction condition, the yield of lactic acid from xylan was only ~15%. Therefore, the extent of depolymerization of xylan and the corresponding mass transfer limitations cannot be excluded that lead to a much lower lactic acid yield from xylan than that from xylose if other reaction conditions are kept identical.

4. Conclusions

In summary, we demonstrated that lactic acid was yielded from xylose or xylan in the pH neutral aqueous solutions with the addition of a ZrO₂ catalyst under different reaction conditions. Under the tested conditions (160–240 °C, 0–100% O₂ partial pressure, and 0.5–4 catalyst to biomass weight ratio), the highest lactic acid yields are 42% and 30% from xylose and xylan, respectively, with the ZrO₂ catalyst, while the process without ZrO₂ only yields negligible lactic acid production. Compared to the mono-functional base catalyst like MgO, the bi-functional ZrO₂ is superior towards the lactic acid synthesis from xylose. We attribute that the acid/base pairs on the ZrO₂ surface facilitate the retro-aldol condensation of xylose, which is the initial step of the conversion of xylose to lactic acid. Through the probe reactant studies, we conclude that ZrO₂ also catalyzes the transformation of xylose derived C3 aldehydes into lactic acid. The conversion of xylan is significantly more challenging than that of xylose and thus requires more severe process conditions such as higher temperatures, longer reaction times, and higher amounts of catalyst loading. The suppression of the catalytic activity of ZrO₂ by the acetyl groups in xylan is minimal, while the polymeric structure mainly contributes to the lower yield production of lactic acid from xylan than that from xylose. Overall, this aqueous catalytic process using the ZrO₂ catalyst is renewable and environmentally-friendly to produce lactic acid from hemicellulosic biomass feedstocks.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2014.06.025>.

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